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HIGH-ACTIVITY CALCIUM OXIDE POROUS BODY AND ITS PRODUCTION

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(54) [Title of the Invention]

High-Activity Calcium Oxide Porous Body and Its Production

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[Scope of Patent Claims]

[Claim 1] A high-activity calcium oxide porous body comprising a granulated body calcined product of calcium hydroxide or calcium carbonate having a specific surface area of at least 5 m<sup>2</sup>/g and a particle diameter of at least 1 mm.

[Claim 2] A method for producing the high-activity calcium oxide porous body as described in Claim 1, characterized in that a calcium hydroxide powder of 300 μm or less in particle diameter is granulated to granules of at least 1 mm in particle diameter, and this granulated body is heated under normal pressure, heated between 390 ~ 480° C in at least 5 min, and then calcined.

[Claim 3] A method for producing the high-activity calcium oxide porous body as described in Claim 1, characterized in that a calcium hydroxide powder of 300 μm or less in particle diameter is granulated to granules of at least 1 mm in particle diameter, this granulated body is heated under normal pressure,

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<sup>1</sup>Numbers in the margin indicate pagination in the foreign text.

heated between 390 ~ 480° C in at least 5 min, and then calcined at an optional temperature within the range of 480 ~ 950° C for a time within a range where the CO<sub>2</sub> reaction ratio is not decreased to below 40 %.

[Claim 4] A method for producing the high-activity calcium oxide porous body as described in Claim 1, characterized in that a calcium hydroxide powder of 300 μm or less in particle diameter is granulated to granules of at least 1 mm in particle diameter, and this granulated body is heated under normal pressure, heated between 700 ~ 780° C in at least 5 min, and then calcined.

[Claim 5] A method for producing the high-activity calcium oxide porous body as described in Claim 1, characterized in that a calcium hydroxide powder of 300 μm or less in particle diameter is granulated to granules of at least 1 mm in particle diameter, this granulated body is heated under normal pressure, heated between 700 ~ 780° C in at least 5 min, and then calcined at an optional temperature within the range of 780 ~ 950° C for a time within a range where the CO<sub>2</sub> reaction ratio is not decreased to below 40 %.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application] The present invention relates to a high-activity calcium oxide porous body having a large specific surface area, a large particle size, and being easy to handle and relates to its production method.

[0002]

[Prior Art] Calcium oxide is usually produced by calcining calcium carbonate; however, it has been known that the activity depends upon the calcination temperature. Namely, calcium oxide obtained at a calcination temperature close to the decarbonization temperature of calcium carbonate is called soft burned quick lime and is rich in activity. Calcium oxide burned at an even higher temperature is called hard burned quick lime and has low activity. This is because of the open porosity, in other words, the decrease of specific surface area due to growth and burning up of the crystal of calcium oxide. For instance, the open porosity is about 50 % and the specific surface area is about  $2 \text{ m}^2/\text{g}$  for a pure product, while the open porosity of the hard burned quick lime is about 10 % and the specific surface area becomes as small as about  $0.04 \text{ m}^2/\text{g}$  for the hard burned quick lime.

[0003] Attempts at reducing the fineness and increasing the specific surface area have been made so far to obtain a high-activity calcium oxide porous body; however, there is a

limitation on reducing the powder of calcium carbonate. Therefore, the specific surface area cannot be increased too much so long as calcium carbonate is used as a starting material, thus the maximum specific surface area of calcium oxide powder due to calcination at normal pressure is about 3 m<sup>2</sup>/g. Although it has been proposed to increase the activity by calcination under vacuum, the method has many problems with equipment and has not been used in practice yet [*Gypsum & Lime*, No. 178, pp 31 ~ 40].

[0004] On the other hand, an example wherein a fine powder of calcium hydroxide was used as a raw material and calcined at a temperature of 300 ~ 390° C under vacuum to produce a calcium oxide powder having a large specific surface area of 110 ~ 133 m<sup>2</sup>/g has also been known [*Journal of the American Ceramic Society (J. Am. Ceramic Soc.)*, 64 (2), pp 74 ~ 80]; the powder obtained by this method is high-activity and has a particle diameter as fine as 1 ~ 10 μm; therefore, it is hard to handle and its application field is unavoidably limited.

[0005]

[Problem to Be Solved by the Invention] The present invention was made to provide a high-activity calcium oxide porous body having a large specific surface area and thus having a high activity, a large particle size, and being easy to

handle; therefore, it is usable over a wide range, for example, catalysts, adsorbents for exhaust gas, heat insulating materials for steel making, fluxes for steel making, and so on.

[0006]

[Means for Solving the Problem] The inventors repeated earnest studies to obtain a high-activity calcium oxide; consequently, they discovered that a calcium oxide porous body obtained by granulating a calcium hydroxide or a calcium carbonate fine powder and then calcining it at a comparatively low temperature under predetermined heating conditions exhibited high activity even if it has a large particle size. Thus, they came to accomplish the present invention on the basis of this knowledge.

[0007] Namely, the present invention provides a high-activity calcium oxide porous body comprising a granulated body calcined product of calcium hydroxide or calcium carbonate having a specific surface area of at least  $5 \text{ m}^2/\text{g}$  and a particle diameter of at least 1 mm.

[0008] According to the present invention, such a high-activity calcium oxide porous body can be produced by granulating a calcium hydroxide powder of 300  $\mu\text{m}$  or less in particle diameter to granules of at least 1 mm in particle diameter, heating this granulated body under normal pressure,

heating between 390 ~ 480° C in at least 5 min, or granulating a calcium hydroxide powder of 300 µm or less in particle diameter to granules of at least 1 mm in particle diameter, heating this granulated body under normal pressure, heating between 700 ~ 780° C in at least 5 min, and, if necessary, further calcining at a temperature of up to 950° C for a time within a range where the CO<sub>2</sub> reaction ratio is not decreased to below 40 %.

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[0009] At this time, a commercial calcium hydroxide (slaked lime) may be used as calcium hydroxide used as a raw material, or a hydrated product of commercial calcium oxide (quick lime) can also be used; however, calcium oxide having a purity as high as possible is preferable, because the activity of obtained calcium oxide reduces if impurities are mixed. This calcium oxide is used as a powder of 10 ~ 300 µm in mean particle diameter.

[0010] A commercial product of either light or heavy calcium carbonate may be used as it is, and a calcium carbonate obtained by allowing carbon dioxide to pass through an aqueous calcium hydroxide solution may also be used.

[0011] Next, granulation of calcium hydroxide powder or calcium carbonate powder is carried out by adding water to it, blending, and then extrusion molding it to columnar granules of,



for example, about 3 ~ 6 mm in diameter, about 3 ~ 6 mm in length, and at least 1 mm in minimum diameter by using a conventional granulator. The amount of water added at this time is suitably within the range of 5 ~ 25 wt % based on the weight of calcium hydroxide. An organic binder can also be added as desired to improve the shape retention during this granulation. A water-soluble polymeric substance such as carboxymethyl cellulose (CMC), polyvinyl alcohol, or the like is used as this organic binder. The amount of this organic binder is suitably within the range of 0.5 ~ 5 % per weight of calcium hydroxide.

[0012] Next, the granulated body obtained in this manner is calcined, for example, by an electric furnace. In the case of calcium hydroxide, it must be heated within the range of 390 ~ 480° C in at least 5 min; in the case of calcium carbonate, it must be heated within the range of 700 ~ 780° C in at least 5 min. When the granulated body is calcined under conditions other than those, a high-activity calcium oxide or calcium carbonate having a specific surface area of 5 m<sup>2</sup>/g or more cannot be obtained.

[0013] The heating rate at this time is preferably within the range of 1 ~ 10° C/min. If the temperature comes to the upper limit of 480° C in the case of calcium hydroxide or the upper limit of 780° C in the case of calcium carbonate, the heating is

preferably stopped as quickly as possible. If a pore distribution spectrum is measured, a peak is found in the vicinity of  $0.02 \sim 0.2 \mu\text{m}$  at this point of time.

[0014] In a large quantity treatment, the heating must be continued to estimate complete calcination of charged materials. In this case, attention must be paid so that the temperature does not exceed  $950^{\circ}\text{C}$ , and the  $\text{CO}_2$  reaction ratio cannot be less than 40 %. For instance, it is carried out by pulling out a sample every predetermined elapsed time and measuring the  $\text{CO}_2$  reaction ratio of this sample.

[0015] If this heating time is too long and the  $\text{CO}_2$  reaction ratio becomes a state of below 40 %, coagulation of activity calcium oxide obtained occurs, the activity starts to reduce, and the time increases, and this tendency becomes significant as time increases.

[0016] A gas mixture of  $\text{CO}_2$  and  $\text{N}_2$  having the  $\text{CO}_2$  concentration known beforehand in a sample is brought into contact at  $20^{\circ}\text{C}$  for 1 min, and the  $\text{CO}_2$  reaction ratio in the present invention is defined as a difference of  $\text{CO}_2$  concentrations before and after contact divided by the  $\text{CO}_2$  concentration before contact and multiplied by 100.

[0017] In the above calcination, the calcination time can be shortened by adding a reductant decomposed at a low

temperature, such as calcium fluoride. According to the invented method, a calcium oxide having activity adjusted to a desired extent can be obtained by selecting the above production condition.

[0018] In this manner, a high-activity calcium oxide porous body having a specific surface area of  $5 \text{ m}^2/\text{g}$  or more and high activity of commonly  $10 \sim 60 \text{ m}^2/\text{g}$  is obtained as a granulated body of  $1 \sim 6 \text{ mm}$  in diameter. This porous body is crushed more finely as necessary for various purposes.

[0019]

[Effects of the Invention] The invented calcium oxide has an advantage of being very easy to handle because it has a large specific surface area of at least  $5 \text{ m}^2/\text{g}$ , exhibits a very high activity, and is a porous body, and it can be utilized in catalysts, exhaust gas absorbents, an insulating material for steel making, and a flux for steel making as a product having a particle size larger than conventional calcium oxide. The invented method also has an advantage that it can give a calcium oxide having activity corresponding to use purposes by selection of production conditions.

[0020]

[Embodiments] Next, the present invention is described in more detail by embodiments. The CO<sub>2</sub> reaction ratio and the specific surface area are obtained as follows.

(1) CO<sub>2</sub> reaction ratio: 5 g of a sample was charged into a cylindrical reactor of 20 mm in inside diameter and 600 mm in length, a mixture of CO<sub>2</sub> gas and N<sub>2</sub> gas was allowed to pass through it at a rate of 100 mL/min at a temperature of 20° C, the CO<sub>2</sub> concentration in mixtures before and after contact with the sample was measured by JIS R6124 combustion volume method, and the CO<sub>2</sub> reaction ratio was calculated from the obtained result according to the following expression.

[0021]

[Equation 1] [the expression is missing here, translator]

[0022] (2) Specific surface area: 0.5 g of each sample was measured by a Monothorp specific surface area measurer (made by Yuasa Ionics Co.) according to BET common point (shuten) method, and then the measured value was doubled and taken as the surface area per 1 g.

[0023] Embodiment 1

25 wt % of water was added to a calcium hydroxide powder (an industrial slaked lime made by Suzuki Industry Co., Ltd., purity 95.9 %, particle size 300 μm or less) to granulate it

into granules of 3 mm in diameter and 3 mm in length by a disk pelleter (made by Fuji Powder Co., Ltd.).

[0024] This granulated body was put into an electric

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furnace, heated to 470° C at a heating rate of 1° C/min, when its temperature reached 470° C was withdrawn immediately from the electric furnace, and then was cooled. The heating time from 390° C to 480° C at this time was 90 min.

[0025] When the pore distribution of this body was measured by a pore distribution meter (Poresizer 9310, made by Micromedics Co., Ltd.), a maximum peak was found at a position of 0.06  $\mu\text{m}$ . The CO<sub>2</sub> reaction ratio of this powder was 97 %, and the specific surface area was 57.67 m<sup>2</sup>/g.

[0026] Embodiment 2

A calcium hydroxide powder [made by Bihoku Pulverization Co., Ltd., purity 98 %, particle size 150  $\mu\text{m}$  or less] was granulated into granules of 3 mm in diameter and 3 mm in length. This granulated body was put into an electric furnace, heated from room temperature to 780° C at a heating rate of 1° C/min, when the temperature reached 780° C was withdrawn simultaneously from the electric furnace, and then was cooled. The heating time from 700° C to 780° C at this time was 80 min. The CO<sub>2</sub> reaction

ratio of this body was 95 %, and the specific surface area was 35.86 m<sup>2</sup>/g.

[0027] Embodiments 3 ~ 6

A calcium hydroxide powder [an industrial slaked lime, purity 95.9 %, made by Suzuki Industry Co., Ltd.] was classified as fractions of 45 μm and under, 45 μm ~ 75 μm, 75 μm ~ 150 μm, and 150 μm ~ 300 μm, 25 wt % of water was added to each fraction to granulate it into granules of 3 mm in diameter and 3 ~ 4 mm by a disk pelleter [made by Fuji Powder Co., Ltd.], this granulated body was heated to 700° C at a heating rate of 10° C/min, and then it was calcined for 1 hr at a heating temperature of 900° C. The CO<sub>2</sub> reaction ratio and the specific surface area of the calcium oxide porous body obtained in this manner were measured. This result is shown in Table 1.

[0028]

[Table 1]

試 料	フラクションの粒度	比表面積 (m <sup>2</sup> / g)	CO <sub>2</sub> 反応率 (%)
実施例3	45 μm以下	20.02	92.53
実施例4	45~75 μm	13.86	95.71
実施例5	75~150 μm	8.92	93.58
実施例6	150~300 μm	7.66	91.18

A	B	C	D
E			
F			
G			
H			

Translator's note:

- A Sample
- B Particle size of fraction
- C Specific surface area ( $\text{m}^2/\text{g}$ )
- D  $\text{CO}_2$  reaction ratio (%)
- E Embodiment 3
- F Embodiment 4
- G Embodiment 5
- H Embodiment 6

[0029] As is evident from this table, all the calcium hydroxide powders having a particle diameter of 300  $\mu\text{m}$  or less give calcium oxide having a specific surface area of 5  $\text{m}^2/\text{g}$  or more.

[0030] Embodiment 7

The calcium hydroxide powder used in Embodiment 1 was granulated into granules of 3 mm in diameter and 3 mm in length, then this granulated body was put into an electric furnace, heated to 700° C at a heating rate of 10° C/min, and calcined at this temperature for 30 min. The heating temperature from 390° C to 470° C at this time was 8 min. The pore distribution of the calcium oxide porous body obtained in this manner was measured. As a result, it was known that this invention product had a pore range of 0.02 ~ 0.2  $\mu\text{m}$ .

[0031] Embodiments 8 ~ 13, Comparative example 1

The same calcium hydroxide powder used in Embodiment 6 was granulated into granules of 3 mm in diameter and 3 mm in length, then this granulated body was put into an electric furnace, heated to different temperatures from room temperature to 400 ~ 1,100° C at a heating rate of 10° C/min, and each was calcined for 30 min. The heating temperature from 390° C to 470° C at this time was 8 min. The CO<sub>2</sub> reaction ratio and the specific surface area of the calcium oxide porous body obtained in this manner were measured, and the result is shown in Table 2.

[0032]

[Table 2]

試 料	最終加熱温度 (°C)	比表面積 (m <sup>2</sup> / g)	CO <sub>2</sub> 反応率 (%)
実施例8	500	21.41	93.17
実施例9	600	23.68	94.35
実施例10	700	18.53	97.18
実施例11	800	15.84	96.42
実施例12	900	10.41	96.07
実施例13	950	6.97	92.54
比較例1	1100	3.50	52.34

A	B	C	D
E			
F			
G			
H			
I			
J			
K			

Translator's note:



A	Sample
B	Final heating temperature (°C)
C	Specific surface area (m <sup>2</sup> /g)
D	CO <sub>2</sub> reaction ratio (%)
E	Embodiment 8
F	Embodiment 9
G	Embodiment 10
H	Embodiment 11
I	Embodiment 12
J	Embodiment 13
K	Comparative example 1

[0033] Embodiments 14 ~ 16, Comparative example 2

The same calcium hydroxide powder of 150 μm or smaller in particle size used in Embodiment 2 was granulated into granules of 3 mm in diameter and 3 ~ 4 mm in length, this granulated body was heated from room temperature to 800° C, 900° C, 950° C and 1,100° C, at a heating rate of 10° C/min, respectively, and after the temperature reached the maximum temperature, it was calcined for 30 min. Next, each sample was withdrawn from an electric furnace and cooled, the CO<sub>2</sub> reaction ratio and the specific surface area of this porous body were measured, and the result is shown in Table 3.

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[0034]

[Table 3]

試 料	最高加熱溫度 (°C)	比表面積 (m <sup>2</sup> / g)	CO <sub>2</sub> 反應率 (%)
實施例14	800	8.54	93.89
實施例15	900	12.72	97.00
實施例16	950	10.08	95.05
比較例2	1100	4.62	65.21

A	B	C	D
E			
F			
G			
H			

Translator's note:

A Sample

B Maximum heating temperature (°C)

C Specific surface area (m<sup>2</sup>/g)

D CO<sub>2</sub> reaction ratio (%)

E Embodiment 14

F Embodiment 15

G Embodiment 16

H Comparative example 2